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Transition-State Theory of the Linear Rate of Decomposition of Ammonium Perchlorate*

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by

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Abstract

The experimental data of Bircumshaw and Newman are analyzed in terms of a linear rate of progression of the interface between residue and undecomposed crystal. Linear decomposition rates corresponding to given temperatures are derived directly from the maximum rate portions of the sigmoid curves of product pressure versus time. It is proposed that in the temperature range 220°C to 280°C, the decom-

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position interface travels exclusively through the disordered material between the mosaic blocks of the crystal and does not penetrate the interior of these blocks. Absolute rate treatments in the manner of Laidler, Glasstone, and Eyring are presented for each of the two crystal forms (orthorhombic and cubic). These treatments are similar to those proposed for the sublimation of ionic solids and the vaporization of solid ammonium chloride, respectively.

Introduction

Bircumshaw and Newman[1] have recently summarized the results of an exceptionally detailed investigation of the kinetics of decomposition of ammonium perchlorate. The present writers sometime ago obtained a report[2] of well over a hundred pages containing the excellent original data which facilitated the following theoretical analysis. The present paper is based upon a discussion[3] originally presented in 1952 and recently modified in the light of recent studies on the linear vaporiz-

[1] L. L. Bircumshaw and B. H. Newman, Proc. Roy. Soc. (London), A227, 115-132, 228-241 (1954).

[2] L. L. Bircumshaw and B. H. Newman, Interim Report, March, 1951.

[3] R. D. Schultz and A. O. Dekker, "The Kinetics of Decomposition of Ammonium Perchlorate" presented at the 122nd National Meeting, American Chemical Society, Atlantic City, New York, September, 1952.

sation rate of ammonium chloride[4,5] and on the sublimation rates of

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[4] R. D. Schultz and A. O. Dekker, "The Absolute Thermal Decomposition Rates of Solids. Part I," in the Fifth International Combustion Symposium (1954), Reinhold Publishing Company, New York, (1955).

[5] R. D. Schultz and A. O. Dekker, to be published. OSR-TN-55-141.

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molecular[6] and ionic crystals.[7]

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[6] R. D. Schultz and A. O. Dekker, J. Chem. Phys. in press. OSR-TN-54-367.

[7] R. D. Schultz and A. O. Dekker, to be published. OSR-TN-55-138

By a series of excellent photomicrographs on individual crystals of ammonium perchlorate, Bircumshaw and Newman[1] demonstrated that the slow decomposition at 230°C proceeds by the formation of opaque spots (i.e., nuclei) on the crystal surface. These spots then grow in size and eventually coalesce to form a continuous opaque region whose boundary with the transparent region was observed to move uniformly inward toward the center of the crystal. When the boundary reaches the center of the crystal, decomposition ceases, leaving a porous pseudomorph which is still pure ammonium perchlorate but which has a density only 70% of that of the original crystal.

In the following discussion, it is shown that a single consistent treatment of the kinetic data can be made in terms of the linear rate of progression of the interface between partially decomposed and undecomposed crystal. A modification of a treatment by Mott[8] is used to analyze the acceleratory (or nucleation) period, and a modification of a treatment by Topley and Hume[9] is used to analyze the decelerator (or post-coalescence) period. An explanation for the observed cessation of the reaction at 30% completion is proposed on the basis of the concept of mosaic structure in crystals. The experimental linear rates derived by this analysis provide a basis for a transition-state absolute rate treatment in the manner of Glasstone, Laidler, and Eyring. These latter calculations suggest that the intermosaic material of the orthorhombic crystal decomposes below 250°C via a primary rate-controlling step requiring the attainment of nearly free rotation of the perchlorate ion. On the other hand, the intermosaic material of the cubic crystal appears to decompose above 250°C via a rate-controlling step which involves desorption of a loosely bound NH_3:$HClO_4$ complex from its physically adsorbed state at the decomposition interface.

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[8] N. F. Mott, Proc. Roy. Soc. (London), A172, 325 (1939).

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[9] B. Topley and J. Hume, Proc. Roy. Soc. (London), A120, 211 (1929).

Theory of the Nucleation Process in the Accelaratory Period

Hircumshaw and Newman[1,2] have suggested that the formation of centers of decomposition on the crystal surface may be associated with the formation of free adsorbed perchloric acid. To support this hypothesis, they have demonstrated that the induction period for decomposition is considerably shortened by crystallizing some of the salt with perchloric acid as a 2% impurity. Moreover, they find that the induction period is considerably lengthened by a small pressure of ammonia over the salt, presumably caused by the neutralisation of adsorbed perchloric acid. Accordingly, the following mechanism is assumed for the nucleation process:

$$NH_4ClO_4 \underset{b}{\overset{a}{\rightleftharpoons}} NH_3 : HClO_4 \underset{d}{\overset{c}{\rightleftharpoons}} NH_3 + HClO_4 \qquad (1)$$

	(crystal) (surface)	(physically adsorbed surface) complex	(gas)	(adsorbed on surface)
state symbol	(ss)	(ad)	(g)	(ad)

Let ds/dt be the rate of escape of NH_3 (g) from the surface of the crystal in molecules sec^{-1} cm^{-2}. As a first approximation, the back reactions (1b) and (1d) are neglected and reaction (1c) is assumed to be rate controlling, so that

$$\frac{ds}{dt} = k_c (NH_3 : HClO_4)_{ad} = K_s \qquad (2)$$

where k_c is the specific rate constant for reaction (1c) and where K_s

is a combination constant. (The alternate assumption that reaction (1a) is rate-controlling will not affect the mathematical form of the decomposition pressure-time relationship (13) below.) Assume in this first approximation that the rate of escape of perchloric acid from the surface is negligible. Assume also that the time required to attain temperature equilibrium is negligible compared to the duration of the nucleation period. At time t after start of heating, the concentration of perchloric acid in the surface is

$$(HClO_4)_{ad} = s = K_s t \qquad (3)$$

provided that no adsorbed $HClO_4$ or NH_3 is present prior to t = 0. A nucleus will be considered to be in existence when a certain number, j, of $HClO_4$ (ad) molecules have migrated to a potential nucleus site (i.e., surface discontinuity) and have decomposed to leave a surface hole. The mobility of the adsorbed perchloric acid could be the result of a surface lattice migration process of a type discussed by MacDonald.[10] For

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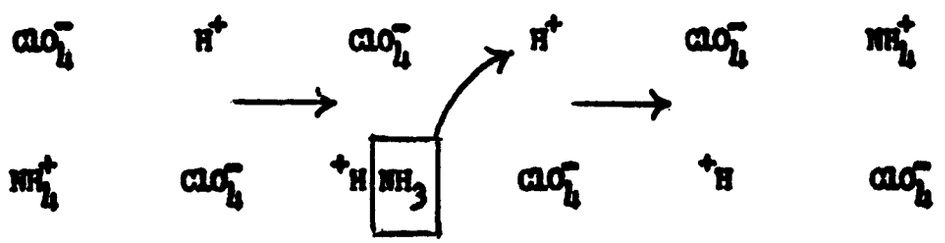
[10] J. Y. MacDonald, Trans. Far. Soc., 47, 860-863 (1951).

NH_4ClO_4 the migration process might be visualized as



(4)

The formation of an empty space in the surface lattice caused by a decomposition reaction of j molecules of $HClO_4$ at a potential nucleus site should loosen the lattice restraints on the immediately adjacent ions, thereby permitting them to enter decomposition reactions. (This situation is comparable to the calcium carbonate decomposition discussed by Langmuir.[11] The latter used the phase rule to show that the lattice vacancy left by the removal of a CO_2 group weakens the bonds by which adjacent groups are held.) The rate of nuclei formation per unit area of crystal is then

[11] I. Langmuir, J. Am. Chem. Soc., 38, 2263-2267 (1916).

$$\frac{dn}{dt} = k_n \gamma s^j = k_n \gamma K_s^j t^j \qquad (5)$$

where γ is the number of potential nucleus sites per unit area and k_n is the specific rate constant of the nuclention process.

It has been observed in many crystal decompositions that the radial growth rate (dr/dt) of a nucleus is constant under isothermal conditions and varies with temperature T according to the equation

$$B = dr/dt = B_o \exp(-E/RT) \qquad (6)$$

At the time τ, the radius of a nucleus born at time t is

$$r = B(\tau - t) \tag{7}$$

Both τ and t are measured from the commencement of heating.

The volume of a hemispherical nucleus is

$$V = (2/3)\pi B^3 (\tau - t)^3 \tag{8}$$

and the total volume V_n of all n nuclei existing at anytime τ before coalescence (i.e., before appreciable interference of decomposition zones occurs) is

$$V_n = \int_0^n (2/3)\pi B^3 (\tau - t)^3 dn \tag{9}$$

where dn is given by equation (5). Hence

$$V_n = \int_0^\tau (2/3)\pi B^3 k_n \gamma K_s^j t^j (\tau - t)^3 dt \tag{10}$$

Integration gives

$$V_n = \frac{4\pi B^3 k_n \gamma K_s^j}{(j+1)(j+2)(j+3)(j+4)} \tau^{j+4} \tag{11}$$

If it is assumed that perchloric acid decomposes by a bimolecular reaction at a potential nucleus site, $j = 2$, so that

$$V_n = (\pi B^3 k_n \gamma K_s^2/90)\tau^6 \qquad (12)$$

In the absence of secondary reactions at time (t), the pressure (p) of decomposition products above the salt is proportional to V_n, so that

$$p = (C\pi B^3 k_n \gamma K_s^2/90)\tau^6 \qquad (13)$$

where C is a constant of proportionality. Equation (13) is identical in form to the power expression, $p = kt^x$ (where $x = 6.2 \pm 0.5$) which Bircumshaw and Newman[2] found to hold for the acceleratory period at 220 - 275°C. Secondary reactions in the gaseous decomposition products which involve volume changes will not affect the experimental value of the exponent x provided that the final decomposition is attained in a time which is either very small or very large compared to the duration of the acceleratory period.

The above calculations suggest that some kind of bimolecular reaction is responsible for the formation of a nucleus but it is by no means certain that the reaction involves perchloric acid. An alternative assumption that a nucleus is formed by two holes (or even two charged particles) which migrate through the crystal lattice and coalesce at a discontinuity in the crystal would lead to a mathematical expression of the same form as equation (13). (See N. F. Mott[8].)

The Maximum Rate Period

Once coalescence of the growing nuclei has occurred so that the surface is completely covered by a layer of residue, equation (13) is no longer valid. At this time, the reaction interfaces no longer increase in area. Instead, the resulting single interface decreases in area as it progresses toward the center of the crystal. Let the shape of a given crystal at coalescence time t_y be approximated as a sphere or radius r_y. The volume V_y of undecomposed crystal inside this sphere at time t_y is

$$V_y = (4/3)\pi r_y^3 \tag{14}$$

At the later time t, the volume V_t of undecomposed crystal is

$$V_t = (4/3)\pi \left[r_y - B(t - t_y) \right]^3 \tag{15}$$

Differentiation gives

$$dV_t/dt = -4\pi B \left[r_y - B(t - t_y) \right]^2 \tag{16}$$

The rate of increase of decomposition product pressure dp/dt is proportional to the rate of volume decrease $-dV_t/dt$ and to Q the number

of crystals assumed uniform in size and shape, so that

$$dp/dt = 4\pi QBG \left[r_y - B(t - t_y) \right]^2 \qquad (17)$$

where G is a proportionality constant. The maximum rate occurs at the time $t = t_y$ so that

$$(dp/dt)_y = 4\pi QBG\, r_y^2 \qquad (18)$$

The number of crystals Q in a fixed initial weight W of uniform NH_4ClO_4 crystals (assumed spherical in shape) is

$$Q = \frac{3W}{4\pi r_o^3 \rho} \qquad (19)$$

where r_o is the initial crystal radius and ρ its density.
Insertion of (19) into (18) gives

$$(dp/dt)_y = 3\,\frac{WBG}{\rho}\,\frac{r_y^2}{r_o^3} \qquad (20)$$

Let the difference between the initial radius of the crystal and the radius of the spherical reaction interface at coalescence be δ so

that

$$r_y = r_o - \delta \tag{21}$$

and

$$(dp/dt)_y \propto (r_o - \delta)^2 / r_o^3 \propto (r_o^2 - 2r_o\delta + \delta^2)/r_o^3 \tag{22}$$

$\propto$ = proportional to

For large crystals, δ is small compared to r_o so that

$$(dp/dt)_y \propto 1/r_o \tag{23}$$

Thus, the maximum rate for a given mass of large NH_4ClO_4 crystals should vary inversely as the initial crystal radius. Indeed, this is nearly the relationship observed by Hircumshaw and Newman[2] for crystals greater than 0.004 inches in diameter. Below this size, the maximum rate was found to decrease with decrease in diameter. This results from the fact that coalescence occurs at greater percentages of decomposition for the smaller particles (i.e., δ is no longer small compared to r_o). Wampel[12]

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[12] K. L. Wampel, Z. Physik. Chem., A187, 43-57, 235-249 (1940).

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reached a similar conclusion about the effect of decreased particle size on the rate of solid decomposition.

For a given batch of uniform crystals, the point of inflection of the commonly observed sigmoid decomposition pressure-time curves correspond approximately to t_y, the time of coalescence of the nuclei on the surface of the crystal. At time $t = t_y$ the decomposition rate, in terms of fraction of original crystal volume V_o, is from equation (16)

$$\left(\frac{dV_t/V_o}{dt}\right)_y = -3B\frac{r_y^2}{r_o^3} \tag{24}$$

But V_o is proportional to p_f, the final decomposition pressure, so that (24) becomes

$$\left(\frac{dp/p_f}{dt}\right)_y = 3B\frac{r_y^2}{r_o^3} \tag{25}$$

The ratio of the volume V_y of undecomposed crystal to the original volume V_o is at time t_y

$$\frac{V_y}{V_o} = \frac{r_y^3}{r_o^3} = \frac{p_f - p_y}{p_f} \tag{26}$$

The radius of the decomposition interface at time t_y is, therefore,

$$r_y = r_o\,(p_f - p_y)^{1/3}\,p_f^{-1/3} \tag{27}$$

The maximum rate of linear progression of the decomposition interface, $B = dr_y/dt$, at time t_y is

$$B = \frac{r_o \, (dp/dt)_y}{3p_f^{1/3} \, (p_f - p_y)^{2/3}} \quad \text{cm sec}^{-1} \qquad (28)$$

where r_o = initial crystal radius — cm

$(dp/dt)_y$ = slope at the point of inflection of sigmoid decomposition product pressure - time curve — mm Hg sec^{-1}

p_y = decomposition product pressure at point of inflection — mm Hg

p_f = final product pressure (assuming no change in volume of system during run) — mm Hg

By means of equation (28), experimental values of B (plotted in Figure 1 as $\log_{10}$ B versus 1/T) were derived directly from the sigmoid p-t curves of the original Bircumshaw and Newman data[2] using their estimated mean value of $r_o = 1.98 \times 10^{-2}$ cm. Below 513°K the linear decomposition rate of the intermosaic material of the orthorhombic NH_4ClO_4 crystal is given by

$$B_{NH_4ClO_4 \text{ (orthorhombic)}} = 1.5 \times 10^8 \exp(-31{,}600/RT) \quad \text{cm sec}^{-1} \qquad (29)$$

At 513°K, the crystal of NH_4ClO_4 assumes the cubic NaCl type lattice. Above this temperature, the linear decomposition rate of the intermosaic material of the cubic NH_4ClO_4 crystal is

$$B_{NH_4ClO_4\ (cubic)} = 2.4 \times 10^{1} \exp(-16{,}200/RT) \quad \text{cm sec}^{-1} \qquad (30)$$

It is of interest to compare equation (29) with an equation[7] recently estimated for the maximum linear rate of advance in vacuo of the decomposition interface between $CaCO_3$ and CaO

$$B_{CaCO_3:CaO} = 7.7 \times 10^{7} \exp(-37{,}600/RT) \quad \text{cm sec}^{-1} \qquad (31)$$

It is also of interest to compare equation (30) with the equation for the linear rate of vaporization of ammonium chloride obtained by an analysis[4] of the experimental data of H. Spingler.[13]

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[13] H. Spingler, Z. Physik. Chem., B52, 90-106 (1942).

$$B_{NH_4Cl} = 1.2 \times 10^{2} \exp(-13{,}500/RT) \quad \text{cm sec}^{-1} \qquad (32)$$

The Decelerator Period

It follows from the previous mathematical analysis that the equation of the decelerator portion of the sigmoid p - t curve is

$$\frac{p_f - p}{p_y} = \frac{\left[r_y - B(t - t_y)\right]^3}{r_o^3} \qquad (33)$$

where r_y is given by equation (27). Figures 2, 3, and 4 compare the decelerator curves derived by equation (33) with the experimental curves. At 215°C, the agreement is excellent but becomes progressively poor with increasing temperature. The discrepancy at higher temperatures may be the result of an increase in the vaporization rate of the salt without oxidization-reduction reactions in the gas phase or perhaps may be the result of an impedance or hindering effect of the layer of residue on the escape of gaseous products from the decomposition interface.

The Thermodynamics of the Simple Dissociation Process

An enthalpy balance for the dissociation of orthorhombic ammonium

perchlorate to gaseous ammonia and perchloric acid may be written as

$$NH_4ClO_4 \rightleftharpoons NH_3 + HClO_4 + \text{heat of reaction} \quad (34)$$

State	(orthorhombic) (crystal)	(gas)	(gas)	
$\Delta H_f^\circ(298^\circ K)$ kcal g-mole^{-1}	-69.4	-11.0	-2.3	-56.0
Reference	14	14	(Calculated)	(By Difference)

14 National Bureau of Standards, Circular 500 (1952).

A value of 8.8 kcal g-mole^{-1} for the enthalpy of vaporization of anhydrous perchloric acid was estimated from vapor pressure data[15] by

15 J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Company, (London), Vol. II, p. 377.

use of the Clausius-Clapeyron equation. This enthalpy of vaporization was added to the -11.1 kcal g-mole^{-1} heat of formation of $HClO_4$ (liq) (Reference 14) to obtain the estimated value ΔH_f° (298°K) $HClO_4$ (gas) $\simeq$ -2.3 kcal g-mole^{-1}. Reaction (34), as written, is endothermic to the extent of about 56 kcal g-mole^{-1}. This value is somewhat uncertain

because the heat of aqueous solution of $HClO_4$ (liq) is not known accurately.[16] Since the endothermicity of the simple dissociation process

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[16] C. F. Goodeve and A. E. L. Marsh, J. Chem. Soc., 1516 (1937).

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(3) is much higher than the observed activation energies for the vaporization process, it follows that the latter must occur in stages rather than as a single step.

The Nature of the Residue

Garner and Hailes[17] have suggested that, in certain cases, solid

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[17] W. E. Garner and H. R. Hailes, Proc. Roy. Soc. (London), A139, 576-595 (1933).

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decomposition might proceed preferentially along the boundaries of the mosaic blocks comprising a crystal. If the decomposition paths at 215 to 280°C travel exclusively through the strained intermosaic lattice in NH_4ClO_4 crystals and do not penetrate the interior of the mosaic blocks, the formation of a residue stable at these temperatures is understandable. The minimum size of the mosaic blocks in ammonium perchlorate may be estimated on the assumption that the thickness of the strained transition lattice is about equal to the side of a unit cell of the cubic lattice.

If the residue consists mainly of the original mosaic blocks with the intermosaic material removed, it follows that

$$\frac{\text{Mass residue}}{\text{Mass original crystal}} = \left[\frac{D}{D+d}\right]^3 = 0.7 \qquad (35)$$

where D is the side dimension of the mosaic block

d is the thickness of the intermosaic layer

0.7 is the fraction of the original mass remaining after cessation of decomposition.

Setting d equal to 7.64 A, the side dimension of the unit cell in cubic NH_4ClO_4 (Reference 18), gives a minimum average value of about 62 A for

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[18] K. Herrmann and W. Illge, Z. Krist, 75, 41-66 (1931).

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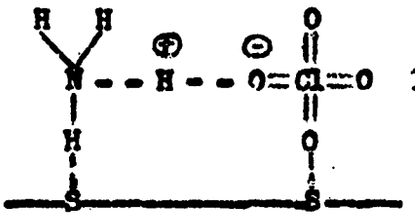
the side dimension of a mosaic block or about 69 A for the spacing of successive intermosaic layers.

Transition State Decomposition Rate Theory for Intermosaic Cubic NH_4ClO_4

Assume that the final stages of the mechanism of decomposition of the intermosaic material in the cubic form of ammonium perchlorate is



$$\xrightleftharpoons[b]{a} NH_3(gas) + HClO_4(gas) + S_2 \qquad (36)$$

(37)

Reaction Intermediate — Irreversible Oxidation-Reduction

where S_2 is a dual adsorption site and where the reaction intermediate is a loose $NH_3 : HClO_4$ complex which is physically adsorbed at the decomposition interface. Reactions (36a) and (36b) are similar to those assumed in a recently revised absolute rate treatment[5] of the ammonium chloride decomposition $NH_4Cl(s) \rightleftharpoons NH_{3(g)} + HCl_{(g)}$. A possibility exists, therefore, of analyzing the reverse reaction (36b) by a straightforward application of the absolute rate treatment formulated by Laidler, Glasstone, and Eyring[19] for a bimolecular surface reaction

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[19] See K. J. Laidler, "The Absolute Rates of Surface Reactions" in Catalysis, Vol. I, Part 1, 195-243 (1954); P. H. Emmet, editor. Reinhold Publishing Co., New York. See particularly pp. 214-217.

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proceeding by Langmuir-Hinshelwood mechanisms. By analogy with the treatment for NH_4Cl, the maximum exchange rate, reaction (36b), should be equal to the maximum forward rate of reaction (36a). Assuming the latter to be rate-controlling, the maximum decomposition rate of the

intermosaic material of the cubic form of ammonium perchlorate should correspond to the equation

$$\frac{-d(NH_4ClO_4)}{dt} = \left[NH_3\right]_g \left[HCl\right]_g \; C_{S_2} \; \frac{kT}{h} \; \frac{F^*}{F_{NH_3(g)} F_{HCl(g)} F_{S_2}} \; e^{-E_o/RT} \qquad (38)$$

ion-pairs
$cm^{-2}\ sec^{-1}$

where

$-d(NH_4ClO_4)/dt$ = the decomposition rate per unit area of exposed surface of intermosaic material — ion-pairs $cm^{-2}\ sec^{-1}$

$\left[NH_3\right]_g$ = steady state gas phase concentration of ammonia in contact with the reaction interface — molecules cm^{-3}

$\left[HClO_4\right]_g$ = steady state gas phase concentration of perchloric acid in contact with the reaction interface — molecules cm^{-3}

C_{S_2} = concentration of bare dual adsorption sites — cm^{-2}

F^* = partition function of activated complex over all degrees of freedom except the vibrational mode included in kT/h

$F_{NH_3(g)}$ = partition function of ammonia per unit volume of gas phase

$F_{HClO_4(g)}$ = partition function of perchloric acid per unit volume of gas phases

f_{S_2} = partition function of a bare dual adsorption site

E_o = activation energy of surface reaction — calories g-mole^{-1}

kT/h = Eyring frequency for passage over potential energy barrier — sec^{-1}

By a procedure nearly identical to that used for ammonium chloride[5] equation (38) may be simplified to

$$R_{NH_4ClO_4\ (cubic)} = \left(\frac{M}{\rho N}\right)^{1/3} \frac{kT}{h} \frac{f^*\ (trans)}{f\left(\nu_{NH_3}\right) f\left(\nu_{HClO_4}\right)} e^{-\left(E_o + E_{NH_3} + E_{HClO_4}\right)/RT} \qquad (39)$$

where

kT/h = Eyring transition-state frequency for passage over a potential energy barrier — sec^{-1}

M = formula weight of NH_4ClO_4 — g g-mole^{-1}

ρ = density of NH_4ClO_4 (cubic) $\simeq$ 1.95 — g cm^{-3}

N = Avogadro's number — molecules g-mole^{-1}

f^* (trans) = partition function for a one-dimensional translation motion of the center of gravity of the complex in the plane of the crystal surface. As an approximation f^* (trans) $\simeq 1$

$f(\nu)$ = single mode vibrational partition function of the form $\left[1-\exp(-h\nu/kT)\right]^{-1}$. As an approximation $f(\nu) \simeq kT/h$

ν_{NH_3}, ν_{HClO_4} = frequencies for translational oscillation of physically adsorbed ammonia and hydrogen chloride in the plane of the adsorbed layer at the decomposition interface — sec^{-1}

E_o = activation energy for surface reaction — calories g-mole^{-1}

E_{NH_3} = energy of adsorption of ammonia — calories g-mole^{-1}

E_{HClO_4} = energy of adsorption of perchloric acid — calories g-mole^{-1}

Implicit in equation (39) is the assumption that the rotational oscillation of physically adsorbed $HClO_4$ is nearly free gas-type rotation. The frequencies ν_{NH_3} and ν_{HClO_4} may be estimated in the manner of Hill[20]

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[20] T. L. Hill, J. Chem. Phys., 16, 181-189 (1948).

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and Drenan and Hill[21] by use of the equation

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[21] J. W. Drenan and T. L. Hill, J. Chem. Phys., 17, 775-781 (1949).

$$\nu = (v_o/ma^2)^{1/2} = 1.025 \times 10^{13} \ (V_o/MS^2)^{1/2} \quad \text{sec}^{-1} \quad (39)$$

where

$\nu = \nu_x = \nu_y$ = translational oscillation frequency in the x or y directions in the plane of the physically adsorbed layer — sec^{-1}

v_o = maximum potential energy barrier to translation in x or y direction — ergs

m = mass of adsorbed molecule — g

a = distance between potential minima along x or y axis of surface lattice (assumed simple cubic) — cm

V_o = same as v_o except for unit — kcal g-mole^{-1}

M = molecular weight of adsorbed molecule — g g-mole^{-1}

S = same as a except for unit — Å

Hill[20] has estimated the potential barrier V_o to be about 0.3 - 1.0 kcal g-mole. If $HClO_4$ is adsorbed preferentially on a NH_4^+ ion and

NH_3 is adsorbed preferentially on a ClO_4^- ion, the distance S should be about equal to the 7.64 Å side dimension of the unit cell in cubic NH_4ClO_4. Thus, the estimated frequencies are

$$\nu_{NH_3} \cong 1.8 \text{ to } 3.3 \times 10^{11} \qquad \text{sec}^{-1} \quad (40)$$

$$\nu_{HClO_4} \cong 0.7 \text{ to } 1.3 \times 10^{11} \qquad \text{sec}^{-1} \quad (41)$$

As in the treatment for ammonium chloride

$$E_o \cong 2V_o \cong 600 \text{ to } 2000 \qquad \text{calories g-mole}^{-1} \quad (42)$$

$$E_{NH_3} \cong \Delta H_{cg\ NH_3} - RT_{cg} \cong 6460 \qquad \text{calories g-mole}^{-1} \quad (43)$$

$$E_{HClO_4} \cong \Delta H_{cg\ HClO_4} - RT_{cg} \cong 10{,}700 \qquad \text{calories g-mole}^{-1} \quad (44)$$

where ΔH_{cg} signifies an enthalpy of sublimation measured at the temperature T_{cg}. Therefore, the theoretical value of $B_{NH_4ClO_4\ (cubic)}$ at $T_{average} = 532^\circ K$ is between

$$B_{NH_4ClO_4(cubic)} = 5.5 \times 10^{1} \exp(-17{,}800/RT) \qquad \text{cm sec}^{-1} \quad (45)$$

Theory (V_o assumed to be 0.3 kcal g-mole^{-1})

and

$$B_{NH_4ClO_4(cubic)} = 1.8 \times 10^2 \exp(-19{,}200/RT) \quad \text{cm sec}^{-1} \quad (46)$$

Theory (V_o assumed to be 1.0 kcal g-mole^{-1})

in fair agreement with the experimentally derived value

$$B_{NH_4ClO_4(cubic)} = 2.4 \times 10^1 \exp(-16{,}200/RT) \quad \text{cm sec}^{-1} \quad (47)$$

Experiment

Use of energies of liquefaction instead of energies of sublimation to approximate E_{NH_3} and E_{HClO_4} would have given an activation energy of 13,900 to 15,500 calories g-mole^{-1} also in fair agreement with the experimental value. In these calculations the enthalpies of sublimation and liquefaction of ammonia were taken from a compilation by the U. S. Bureau of Standards.[22] The enthalpy of fusion of perchloric

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[22] U. S. Bureau of Standards, Circular 500 (1952).

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acid was estimated to be about 2.5 kcal g-mole^{-1} by comparison with nitric, sulfuric, and phosphoric acid. The enthalpy of vaporization of perchloric acid was estimated above to be 8.8 kcal g-mole^{-1} from vapor pressure data at 16 and 39°C.

Transition-State Decomposition Rate Theory for Intermosaic Orthorhombic NH_4ClO_4

For the linear decomposition of the intermosaic material in orthorhombic NH_4ClO_4, the experimentally derived pre-exponential factor of 1.5×10^8 cm sec^{-1} is about the same as for sublimation of simple ionic crystals and for the decomposition of calcium carbonate.[7] In these cases, the chief statistical difference between the initial and activated states appears to be that rotation or nearly free rotation is possible only in the activated state. Accordingly, it will be assumed that the formation of the activated complex for the decomposition of intermosaic orthorhombic NH_4ClO_4 requires the attainment of an almost free rotational motion of the ClO_4^- ion at the decomposition interface. A reasonable estimate of the initial state torsional oscillation frequency of the ClO_4^- ion is about 7.5×10^{12} sec^{-1} corresponding to a characteristic temperature $\Theta = h\nu/k = 360^\circ K$. It will be assumed, in accordance with a suggestion by Dircumshaw and Newman,[1] that the ammonium ion is rotating almost freely in the initial state in both orthorhombic and cubic NH_4ClO_4. Apropos of this assumption, the neutron diffraction experiments of Levy and Peterson,[23] the infrared spectra

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[23] H. A. Levy and S. W. Peterson, J. Chem. Phys., 21, 366 (1953); J. Am. Chem. Soc., 75, 1536-1542 (1953).

studies of Plumb and Hornig,[24] and the Raman spectra studies of Couture-

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[24] R. C. Plumb and D. F. Hornig, J. Chem. Phys., 21, 366-367 and 1113 (1953).

Mathieu and Mathieu[25] provide evidence that one-dimensional rotation of

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[25] L. Couture-Mathieu and J. P. Mathieu, J. Chem. Phys., 49, 226 (1952).

---

the NH_4^+ ion is possible in the ammonium halides (i.e., NH_4Br, ND_4I, NH_4I) possessing the NaCl-type structure. Moreover, the neutron diffraction experiments[23] provide evidence for appreciable rotatory oscillation of the NH_4^+ ion in ND_4Br. The fact that ClO_4^- is larger than either the Br^- or I^- ion makes nearly free rotation of NH_4^+ ion in crystalline NH_4ClO_4 a distinct possibility.

The attainment of the activated complex for decomposition probably also involves a translational motion of the ClO_4^- ion. In a manner analogous to that used for the escape velocity during sublimation,[6,7] the activated state translational motion of the ClO_4^- ion is divided into three components. The partition function for one of these components is included in the kT/h factor of the Eyring formulation of transition state theory. The other two components are assumed to be normal-state translational lattice vibrations. It is further assumed that the translational lattice vibrations of the NH_4^+ ion remain unaltered during the formation of the activated state.

It is now possible to write an absolute rate expression for the pre-exponential linear decomposition rate factor of intermosaic orthorhombic NH_4ClO_4, identical in form to that used for sublimation of a non-linear molecule, namely

$$B_o\ NH_4ClO_4 = \left(\frac{M}{\rho N}\right)^{1/3} \frac{kT}{h} \frac{\pi^{1/2}\left(\frac{8\pi^2 IkT}{h^2}\right)^{3/2}}{\sigma\left[1 - \exp\left(-\theta/T\right)\right]^{-4}} \qquad \text{cm sec}^{-1} \quad (48)$$

orthorhombic

where $\rho \simeq$ density of NH_4ClO_4 (orthorhombic) $\simeq 1.95$ g cm^{-3}

θ = characteristic temperature for lattice vibration frequency, assuming equal frequencies for translational and torsional oscillation $\simeq 350$ °K

σ = 12 = symmetry number of ClO_4^- ion

I = moment of inertia of ClO_4^- ion = 1.57×10^{-38} g cm^{-2}

T = average temperature = 501 °K

Insertion of the above numerical constants into equation (48) yields

$$B_o\ NH_4ClO_4 \text{ (orthorhombic)} = 4 \times 10^7 \qquad \text{cm sec}^{-1} \quad (49)$$

Theory

in reasonable agreement with the experimentally derived value of 1.5×10^8 cm sec^{-1}.

A theoretical calculation of the activation energy for the linear decomposition of intermosaic orthorhombic NH_4ClO_4 is not possible on the basis of present knowledge.

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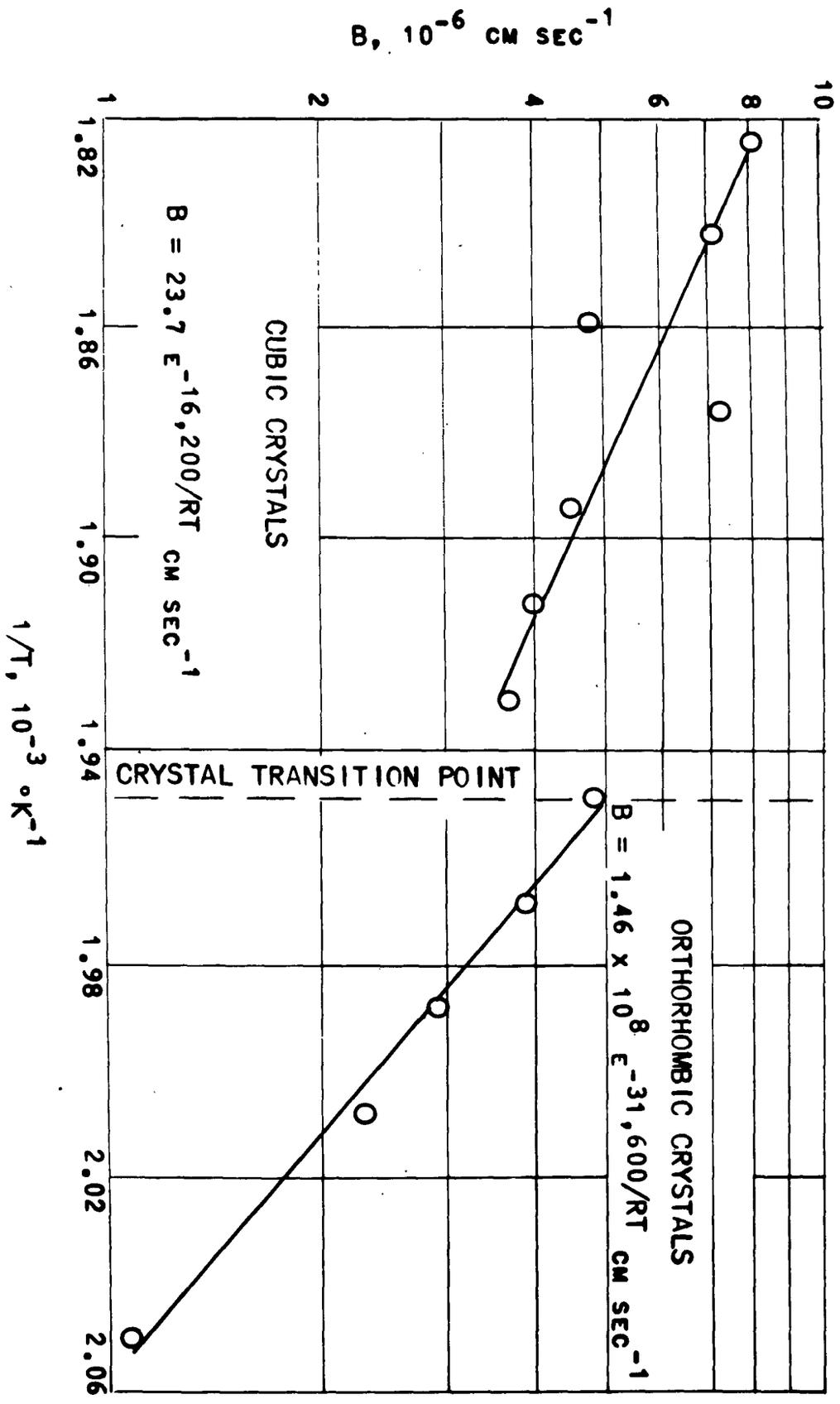
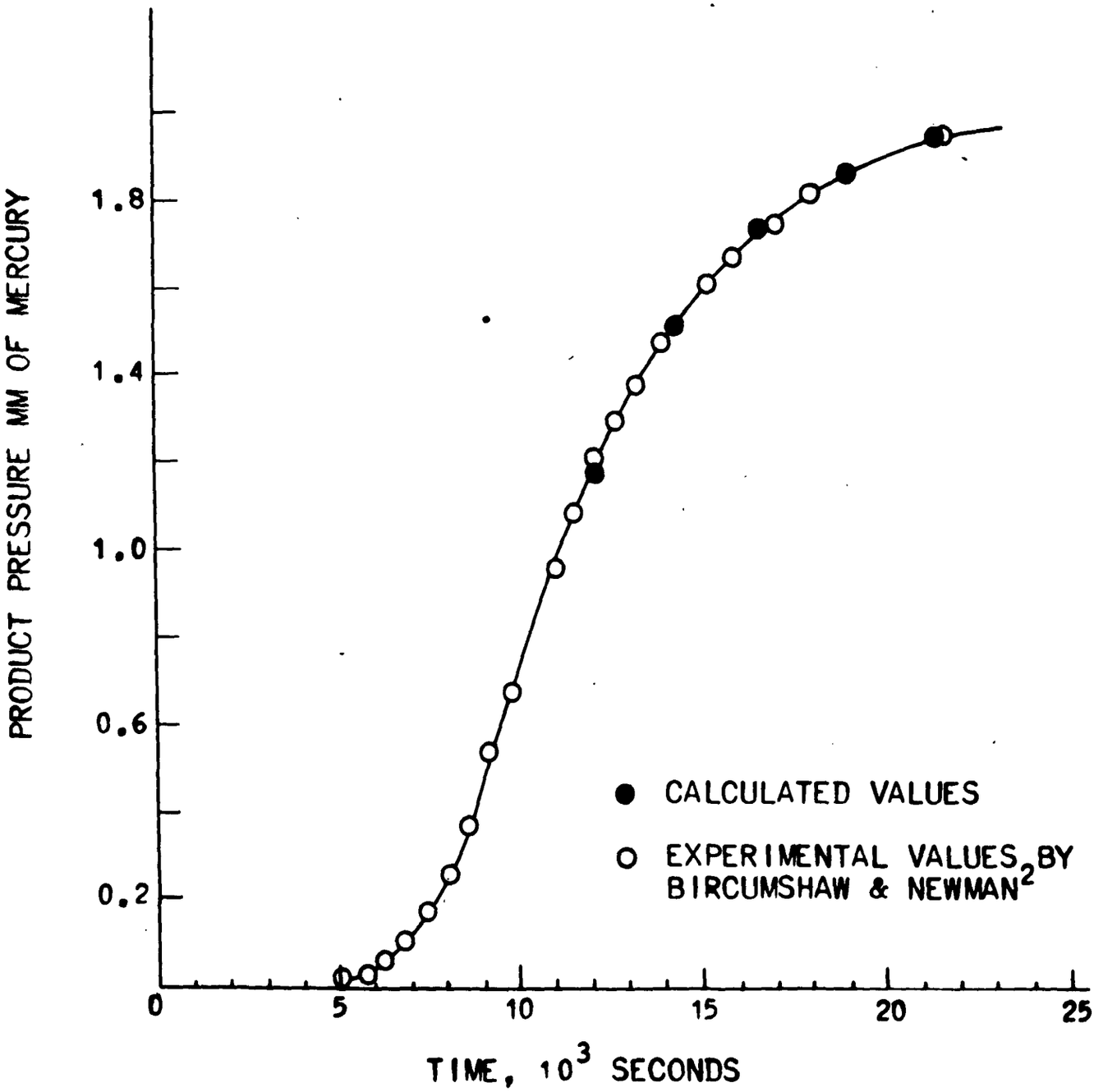
12. Abstract: The experimental data of Bircumshaw and Newman are analyzed in terms of a linear rate of progression of the interface between residue and undecomposed crystal. Linear decomposition rates corresponding to given temperatures are derived directly from the maximum rate portions of the sigmoid curves of product pressure versus time. It is proposed that in the temperature range 220°C to 280°C, the decomposition interface travels exclusively through the disordered material between the mosaic blocks of the crystal and does not penetrate the interior of these blocks. Absolute rate treatments in the manner of Laidler, Glasstone, and Eyring are presented for each of the two crystal forms (orthorhombic and cubic). These treatments are similar to those proposed for the sublimation of ionic solids and the vaporization of solid ammonium chloride, respectively.

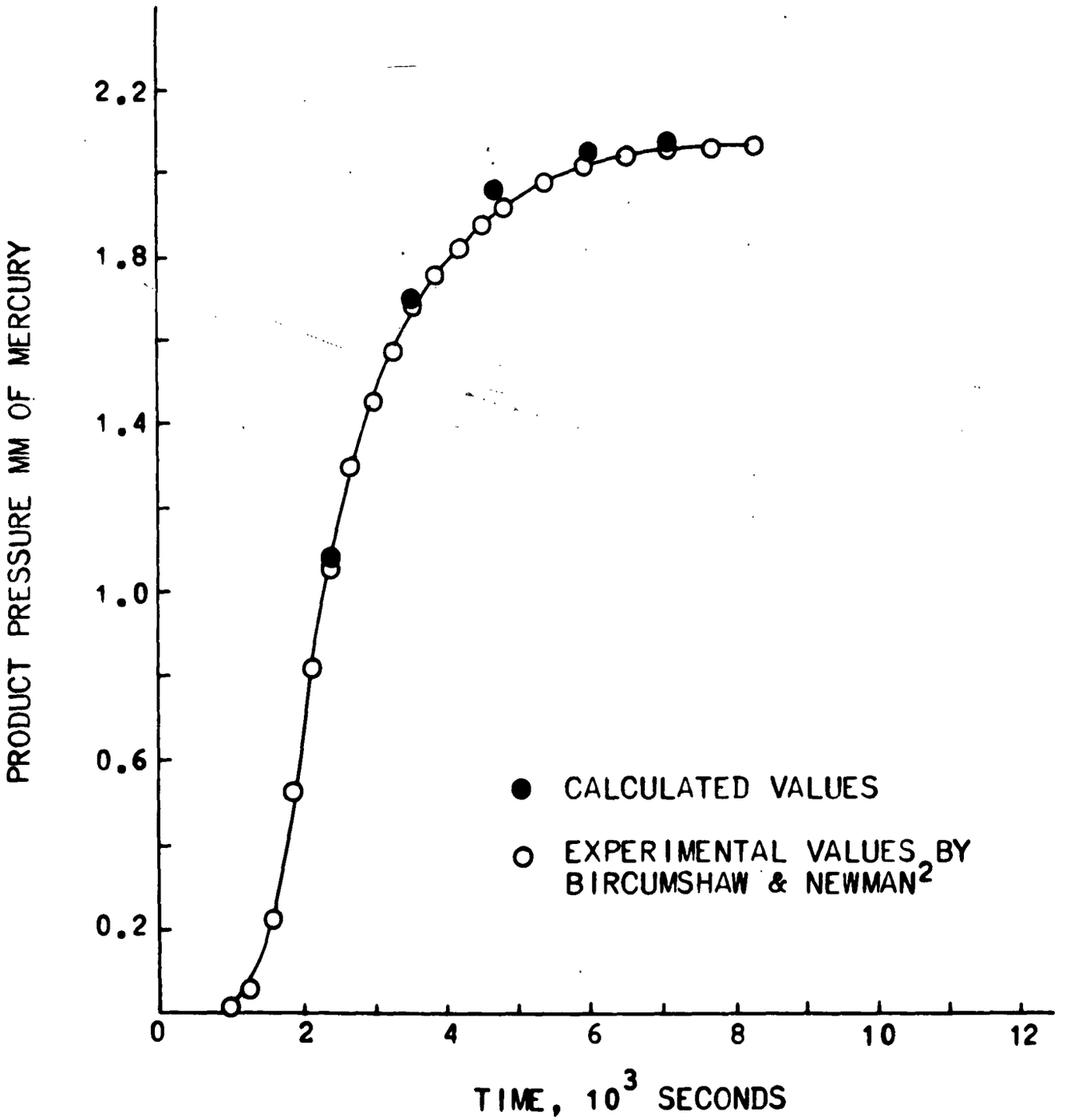


Rate of Linear Progression of Decomposition Interface in Ammonium Perchlorate as a Function of Temperature T

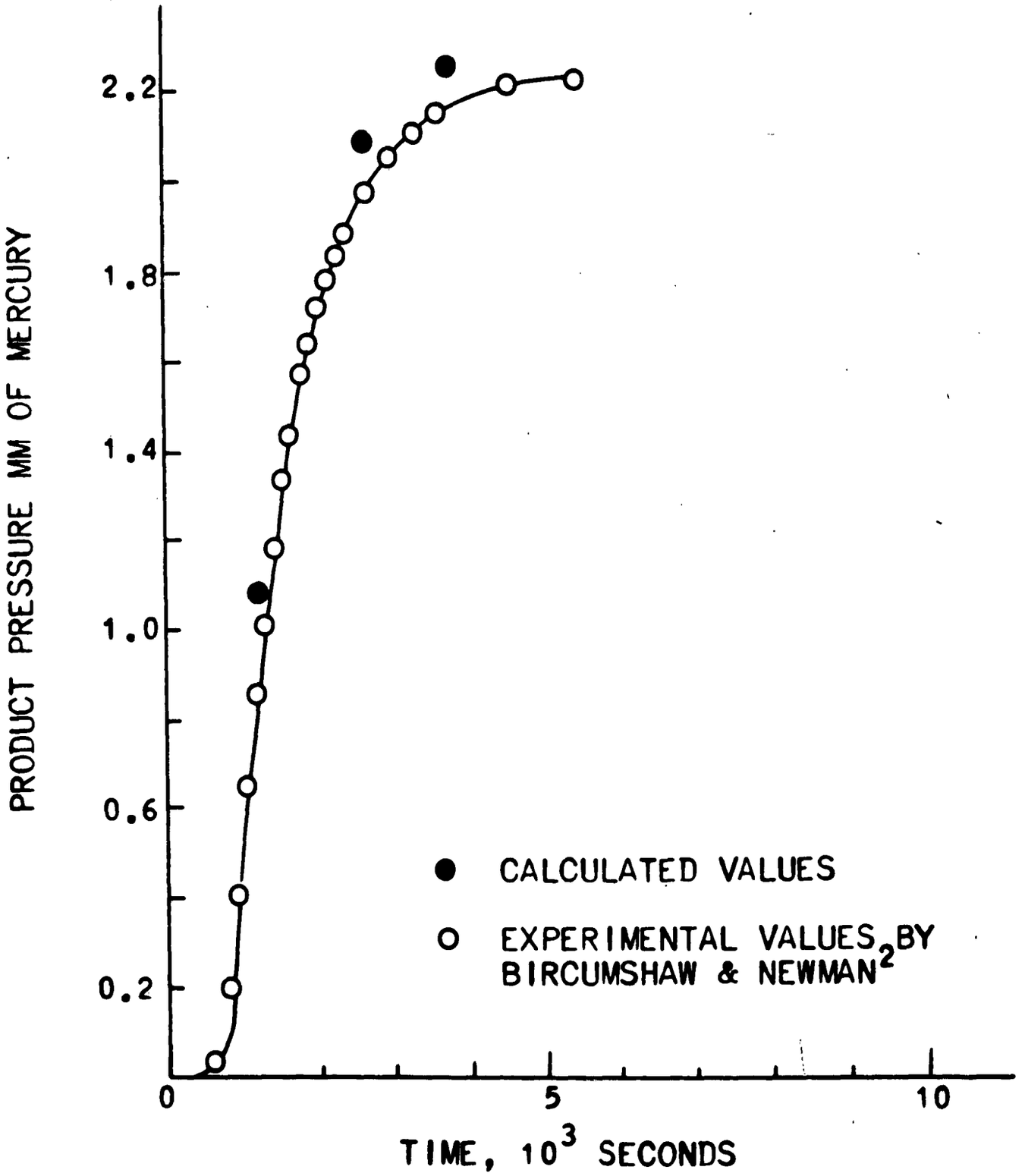
Figure 1



Ammonium Perchlorate Decomposition Curve (215°C) Figure 2



Ammonium Perchlorate Decomposition Curve (250°C) Figure 3



Ammonium Perchlorate Decomposition Curve (270°C) Figure 4

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